

UTILIZATION OF WASTE

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USE OF CHEMICAL WATER PURIFICATION WASTE FROM POWER PLANTS AND MINES IN CERAMIC PRODUCTION

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The possibility of using waste generated by chemical purification of sewage waters from power plants and mines is determined. The main physical properties of the materials obtained are described.

An urgent contemporary problem is recycling large volumes of industrial and household waste, whose discharge into seas and rivers or burial in soil becomes inadmissible. The precipitate of mine water treatment or water purification generated at thermal and nuclear power plants has not yet found application and continues to pollute the environment. Two directions can be distinguished in the utilization of these precipitates:

- use of precipitates as components for ceramic production;
- use of modified precipitates in the industries that can to a maximum degree implement the specific properties of compounds containing iron, nickel, copper, zinc, chromium, and cadmium.

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TABLE 1

Power plants	Mass content, %, in CWT slime					
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	calcination loss
Rostovskaya thermal power plant						
TPP-2	4.8	1.2	2.5	49.7	0.3	41.4
Moskovskaya						
TPP-20	5.1	1.3	1.8	45.8	3.6	42.4
Krasnodarskaya						
TPP	3.9	1.1	2.2	48.7	0.7	37.1
Nesvetai TPP	1.8	1.7	3.1	48.5	3.2	41.7
Novocherkasskaya						
TPP	1.4	1.4	2.6	47.6	4.2	42.8
Voronezhskaya						
TPP	4.7	2.0	4.8	45.3	2.8	38.9

In the production of construction materials it is important to perform binding of the precipitate (slime) with the working mixture components. This will make it possible not only to decrease material consumption and increase the strength parameters of ceramics products but will prevent the wash-out of heavy metal ions [1].

Depending on the purification method, precipitates have different chemical compositions and, consequently, can be used for a wide range of ceramics materials and products.

The chemical composition of slime from power plants after chemical water treatment (CWT) is shown in Table 1 and the averaged chemical composition of slime from CWT of mines is shown in Table 2.

The solid precipitate after treating coal mine water in the Donetsk coal field can be divided into two types; high-iron waste and waste with an increased calcium oxide content.

Along with the study of the chemical composition, a radionuclide analysis of the slime from power plants was carried out. The analysis was performed by the gamma-spectroscopy method on a RÉUS-P-15 radiometric set certified by the TsMII VNIIFGRI Institute of the State Standardization Committee of the Russian Federation as a work analysis of the 2nd rank. The results of the radionuclide analysis of the slime samples from some power plants are shown in Table 3.

TABLE 2

Slime	Mass content, %, in CWT slime from mines					
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	calcination loss
High-calcium	1.9	1.0	2.6	47.4	3.3	43.4
Ferrous	11.4	20.1	27.5	1.5	1.0	38.7

TABLE 3

Power plant	Average specific mass activity of slime, Bq/kg					A_{ef} , Bq/kg
	U = 238	Ra = 226	Th = 232	K = 40	Cs = 137	
Rostovskaya TPP-2	52.0 ± 6.0	8.0 ± 1.0	2.0 ± 1.0	8 ± 1.0	0.2 ± 0.2	9.0
Krasnodarskaya TPP	27.0 ± 10.0	3.5 ± 0.1	4.5 ± 0.4	63.0 ± 25.0	2.9 ± 1.2	9.0
Nesvetai TPP	200.0 ± 10.0	4.7 ± 0.5	3.2 ± 0.3	21.0 ± 2.0	2.7 ± 0.3	11.0
Moskovskaya:						
TPP-11	5.0 ± 3.0	6.0 ± 2.0	2.0 ± 10.0	—	—	10.0
TPP-20	5.0 ± 3.0	9.0 ± 2.0	—	10.0 ± 5.0	—	10.0
TPP-21	9.0 ± 4.0	9.0 ± 1.0	3.0 ± 2.0	13.0 ± 5.0	—	14.0

The actual effective specific mass activity of slime A_{ef} was calculated according to the current Radiation-Hygienic Regulations for building materials of class 1, which should not exceed 370 Bq/kg:

$$A_{ef} = A_{Ra} + 1.31A_{Th} + 0.085A_{K-40} < 370 \text{ Bq/kg.}$$

It can be seen from the data in Table 3 that the slime waste investigated has the actual specific activity significantly below the normal activity prescribed for building materials of class 1; therefore, they are suitable for the production of ceramic materials of class 1 without the need for radioactivity regulation.

The high-calcium waste of the CWT of power plants and mines constitutes a light yellow highly dispersed material, whose main crystalline phase is calcite with a defective structure and, accordingly, with enhanced reaction capacity. This makes it suitable for the production of faience, majolica, and other building ceramics with relatively low-temperature sintering.

The calcium-bearing waste in our study was used in developing a technology for lime faience to be used in facing tiles and household items, as well as building materials, including bricks.

To intensify the sintering process and to form the required ceramic structure, alkali-silicate materials were introduced into the mixtures [2]. The solid-phase sintering process with the formation of anorthite was observed in the mixtures containing alkaline-earth and alkali components in a ratio equal to 3.4 : 5.8.

As the content of alkali increases, the process is shifted toward liquid-phase sintering, in which mainly calcium orthosilicate is formed, which has a simple insular structure and whose formation easily proceeds in the presence of a substantial quantity of the liquid phase.

According to the results of the experiments performed, the content of the high-calcium oxides in mixtures for faience products is limited to 20% and in mixtures for construction ceramics to 35%, which is related to the necessity of obtaining porous materials in the temperature range around 1000°C.

To involve the high-calcium waste in the solid-phase sintering process, alkali-bearing components were added to the

mixtures as mineralizing agents, such as the waste from lead-zinc ore concentration, nepheline-sienite, etc. The total content of the alkalis did not exceed 3%.

Sintering of the synthesized mixtures leads to the formation of an aggregate of crystalline silicates and calcium aluminosilicates in the ceramics, which yields ceramics with the required properties with respect to its strength, water absorption, etc.

Table 4 lists the main physicochemical properties of products made of the mixtures developed.

To impart a particular exterior appearance to construction products, high-iron waste was used.

High-iron waste contains up to 30% F_2O_3 . X-ray phase analysis identified the presence of x-ray-amorphous compounds of iron in the form of gel-like iron oxides $Fe_2O_3 \cdot nH_2O$ and limonite $\beta-Fe_2O_3 \cdot nH_2O$. Small quantities of Al_2O_3 (up to 1%) and SiO_2 (up to 2%) exist as well in a colloid state, which has a significant effect on their further use. The presence of a substantial quantity of the colorant component (Fe_2O_3) in the high-iron waste made it suitable as a colorant for the red-brown color range in the production of a pigment and later of tinted glazes and engobes.

Integrated physicochemical studies revealed that after heat treatment at 700 – 1000°C in a neutral or oxidizing medium it is possible to synthesize a red-brown pigment resistant up to a temperature of 1000°C. This is related to the presence of a stable form $\alpha-Fe_2O_3$ in the specified temperature interval.

The introduction of 7 – 10% pigment for tinting tile glazes demonstrated that the color of the glaze coating depends on the duration of exposure in the furnace and the pigment has no negative effect on the quality and heat resistance of the glaze layer and meets the requirements of GOST 6141–91. High-iron engobe (20 – 30%) without preliminary

TABLE 4

Mixture	Shrinkage, %	Water absorption, %	Bending strength, MPa
Faience	0 – 0.5	18 – 20	35 – 50
Brick	—	25 – 20	10 – 15
Porous	—	40 – 45	5 – 8

heat treatment was introduced into a clay engobe mixture. The engobe was deposited on freshly molded bricks made of mixtures with lime waste of CWT. Firing was performed in an industrial tunnel furnace at the Aksaisk Brick Works.

The products after firing had a denser sintered surface of a red-brown color concealing white spots and salt traces.

Thus, the integrated use of waste materials from polluted sewage of power plants and mines makes it possible to solve an important economic problem and to replace expensive

raw materials in ceramic production, to lower production cost, and to expand the product range.

REFERENCES

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